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Fluorescent Probe Investigation of a Water-Soluble Polyphosphazene

by

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Fluorescent Probe Investigation of a Water-Soluble Polyphosphazene

by

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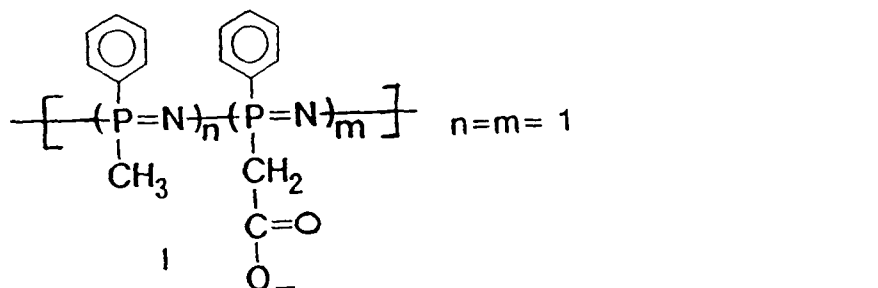
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Abstract

Three fluorescent probes were utilized to investigate the microenvironment created by a water-soluble polyphosphazene copolymer in aqueous solution. The combination of intensity, wavelength shift, and vibrational analysis measurements of the three small molecule probes is used to postulate an environment at high pH (with no added electrolyte) which is similar in polarity to methanol. In the absence of excess small molecule electrolyte, negatively charged probes are repelled by the charge on the polymer. Addition of small molecule electrolyte results in solubilization of the negatively charged probes. However, pyrene, even in the absence of added electrolyte (NaCl), is solubilized. Investigation of pyrene fluorescence quenching demonstrates the ability of the polyphosphazene copolymer to bind positively charged ions (Ti^+) and repel negatively charged ions (I^-). Neutral quenchers such as nitromethane readily penetrate the microenvironment of the polymer.

Introduction

Due to their potential utilization in a variety of applications where water solubility is essential, there is interest in the synthesis and characterization of water-soluble polyphosphazenes. A water soluble (at high pH) copolymer derivative (shown as I below) of poly(methylphenylphosphazene) containing 50% carboxylated functionalities of $\text{CH}_2\text{COO}^-\text{M}^+$ was recently synthesized and characterized by Wisian-Neilson et.al. (1).



In addition, it was determined that the salt derivatives of I in aqueous solutions could be precipitated by addition of a dication salt (CuCl_2), presumably via an ionic crosslinking mechanism.

In view of the novelty of these water-soluble polyphosphazenes, and in anticipation that other equally interesting and potentially useful water-soluble polyphosphazenes might be developed, it is deemed essential to characterize the solution properties of the substituted polymer I. In view of the success in utilizing fluorescent probes to characterize the conformational structure of a number of typical polyelectrolytes [poly(acrylic acid), poly(methacrylic acid), copolymers of maleic anhydride and long chain alkenes, etc.], we have chosen to evaluate the structure of I in aqueous solutions using several luminescent molecules which have been well characterized with respect to their photophysical properties in different environments. Thus three probes, 1-anilino-8-

naphthalene (ANS), 2-p-touilidinylnaphthalene-6-sulfonic acid (TNS), and pyrene, all of which operate by different methods to report on the environment in which they are placed (2-11), are used to gain a realistic description of the carboxylated polyphosphazene polymer I in aqueous solution at high pH.

Experimental

The poly(phosphazene) polymer I was prepared as described previously (1). Pyrene (Aldrich) was purified by column chromatography. ANS (Aldrich) was recrystallized several times from deionized water and TNS (Aldrich) was used as received. KI, CH_3NO_2 , TINO_3 , and dimethylaminopyridine (DMAP) were used as obtained from Aldrich. KOH was used to adjust all aqueous solutions (prepared from deionized water) to a pH of 12. The polymer concentration was kept constant at 0.19 mg/mL. NaCl was obtained from Aldrich. Each sample was degased with N_2 (10min before measuring the fluorescence.) When performing the quenching studies of pyrene, samples were degased for 3 min in between each incremental addition of the quencher before taking the next measurement. Fluorescence spectra (arbitrary units) were recorded on a Spex Fluorolog-2 fluorescence spectrometer. Fluorescence decay curves were measured with a PRA single-photon counting instrument. The nonlinear iterative deconvolution technique was used to fit the decay profiles.

Results and Discussion

The ANS fluorescent probe can exist in the excited single state in two forms, a non-planar state with peak emission maximum (λ_{max}) at 520 nm and a planar intermolecular charge-transfer (CT) state with λ_{max} at 460 nm (3). The medium viscosity and polarity

dictate the relative population of each state and thus the fluorescence spectrum in a given environment. In a polar medium, the emission at 520 nm is enhanced while in a non-polar medium the 460 nm emission predominates. Additionally, the emission at 520 nm in a polar environment is lower than the 460 nm emission in a non-polar environment. These properties of ANS have promoted its use as a reporter of microenvironment for polyelectrolytes such as poly(methacrylic acid) (3) and copolymers of 2-isopropenylnaphthalene (2IPN) and maleic acid (MAA) in aqueous media (2).

Figure 1 shows the fluorescence of ANS ($\lambda_{\text{ex}} = 377 \text{ nm}$) in pure water and in the presence of polymer I (pH=12.0) at several NaCl salt concentrations [the spectra in Figure 1 are corrected for low level anomalous fluorescence from pure polymer/salt solutions]. There is little difference between the fluorescence maximum of ANS in pure water (not shown here) and in an aqueous solution of polymer I with no NaCl added (curve a). Apparently, if there is a hydrophobic microenvironment created by the phosphazene polyelectrolyte, it does not effectively solubilize ANS, at least in the absence of additional indifferent electrolyte such as NaCl. These results are reasonable since, as pointed out by Sturtevant and Webber (2) for the 2-IPN/MAN copolymer system, ANS is negatively charged and in the absence of indifferent electrolyte should experience repulsion by the deprotonated form of I at high pH in pure water. The addition of electrolyte to the solution could well alter the ability of I to provide a stable hydrophobic environment for ANS, and in fact as the concentration of NaCl increases to 0.5 M, the spectra intensify and shift to lower wavelengths. The increase in fluorescence intensity in the solution with the highest NaCl concentration is well over 200% with a peak

maximum at about 470 nm. This is a comparable, if not larger, change to that experienced by ANS in the work reported by Sturtevant and Webber (2) for the 2-IPN/MAA copolymer. The environment, as reflected by the fluorescence wavelength maximum, surrounding ANS is similar to that experienced by the probe in methanol, which has a dielectric constant of 32.7 and a dipole moment of 1.7 Debye (4). The enhanced intensity and blue shift in fluorescence maximum of ANS could result from either a change in the coil with addition of NaCl to form a hydrophobic environment or lowering of the repulsion between ANS and the deprotonated form of I to allow transport into the hydrophobic environment. At this juncture, although we can define the polymer solution of I with high NaCl as providing a somewhat hydrophobic environment, we are still left with the dilemma of defining the microenvironment created by I in aqueous media in the absence of electrolyte. Before attempting to solve this problem, and thus describe the microenvironment of an aqueous solution of I with added electrolyte, we first provide supporting evidence for the hydrophobic environment at high NaCl concentrations.

Additional evidence for the hydrophobic environment created by I in water (pH = 12) is provided by the fluorescence results in Figure 2 for TNS ($\lambda_{\text{ex}} = 345$ nm) in aqueous solutions of I with added NaCl. [The spectra in Figure 2 are corrected for low level anomalous fluorescence from pure polymer/salt solutions]. The wavelength of the fluorescence maximum (435 nm) of TNS, is relatively independent of the salt concentration, but does exhibit the usual increase in intensity (5) typical of TNS in a hydrophobic environment. The absence of fluorescence in an aqueous solution of I with no NaCl added is in excellent agreement with the results for ANS: the same arguments

applied to account for the ANS results can be extended to TNS since TNS is also a negatively charged species and would be expected to be repelled by the deprotonated form of I (at pH=12) upon attempting to enter any hydrophobic environment created by I (in the absence of added NaCl electrolyte).

Having established the hydrophobic nature of the polyelectrolyte I in high pH medium in the presence of added NaCl using two hydrophobic probes TNS and ANS, the task of providing additional information about the hydrophobic microenvironment, particularly in an aqueous solution with no added electrolyte, and its ability to solubilize hydrophobic small molecules remains. Figure 3 shows the fluorescence of pyrene ($\lambda_{\text{ex}}=336$ nm) in pure water plus 0.1M NaCl at pH=12 (curve a) as well as in an aqueous solution (pH=12) of polymer I (curve b). Two observations can be made: first, the overall fluorescence of pyrene intensity increases dramatically in the presence of I and second the relative intensity of the third peak ($\lambda_{\text{em}}=384$ nm) in the vibrational fine structure of pyrene increases with respect to the intensity of the first peak ($\lambda_{\text{em}}=373$ nm), i.e., the 3:1 ratio, increases from 0.55 to 0.79. This increase is indicative of a shift in environment from a purely aqueous medium (dielectric constant of water is 78.54) to a medium with a polarity similar to that of methanol which has a 3:1 ratio of 0.75 (7), and as noted before has a dipole moment of 1.70 Debye and a dielectric constant of 32.7 (4).

Thus, the results for pyrene provide additional insight into the nature of polyphosphazene I in purely aqueous media suggesting that indeed I, in aqueous solution at pH=12, provides a microenvironment which is somewhat hydrophobic (i.e., much like that of methanol) and capable of solubilizing pyrene. The fluorescence decay of the pyrene

probe in aqueous solution at pH=12 (no added NaCl electrolyte) readily fits to a double exponential decay function with lifetimes of 174.2 ns and 360.2 ns and reflects a dual environment, one very polar ($\tau = 174.2$ ns) and one relatively non-polar ($\tau = 360.2$ ns). From the pre-exponential terms used to obtain the double exponential fit to the decay curve, it can be inferred that approximately 83 percent of the pyrene molecules are in the more hydrophobic environment while only about 17 percent are in an aqueous environment. A similar analysis has been applied by Olea and Thomas (11) to account for the multi-environment experienced by pyrene in an aqueous solution of poly(methacrylic acid). Before progressing further in the discussion of the pyrene results in the simple solution of I in water, it should be noted that addition of excess NaCl (up to 0.5 M) did not alter significantly either the 3:1 ratio or the intensity of the pyrene fluorescence (Figure 3, curves c and d). Apparently, even with no added NaCl electrolyte the pyrene probe in the presence of I is in a moderately hydrophobic environment (like that of methanol) which does not change appreciable in its ability to further "solubilize" pyrene. The 3:1 ratio of 0.79 in pH=12 medium in the presence of I is significantly greater than the 3:1 ratio of about 0.55 reported by Olea and Thomas (10) for poly(methacrylic acid) in aqueous solution at pH above 7. Apparently, the phosphazene backbone, even in a high pH medium with the acid functionalities existing as carboxylate salts, is capable of providing a limited hydrophobic microenvironment without added electrolyte (NaCl). The fact that the 3:1 ration remains constant in the presence of 0.5 M NaCl predicts that pyrene is also in a microenvironment similar to methanol: this adds credence to the prediction of a methanol type environment as deduced from the ANS and TNS probe

results discussed previously.

In summarizing the results for the pyrene probe, we conclude that pyrene is capable of detecting the partial hydrophobic nature of the solution of I in the absence of added NaCl. The repulsion argument previously extended to account for the inability of TNS and ANS to interrogate effectively the microenvironment created by I in aqueous media (no added NaCl) seems to be the best explanation of the results in view of the data generated from the pyrene probe analysis. Furthermore, the absence of an appreciable change in pyrene fluorescence intensity or alteration of the 3:1 ratio with added NaCl reflects the static nature of the microenvironment and its lack of dependence on an added electrolyte in further enhancing the hydrophobic nature of the microenvironment created by I.

Additional information about the microenvironment experienced by pyrene in the solution of I in aqueous media can be obtained by quenching the fluorescence of pyrene with a variety of small molecule quenchers, i.e., TiNO_3 , CH_3NO_2 , KI, and DMAP (4-dimethylaminopyridine), each of which is capable of producing a different degree of quenching, depending upon environmental considerations. Figures 4 and 5 show Stern-Volmer (see equation below) plots of pyrene fluorescence intensity (384 nm) as a function of quencher

$$I_0/I = 1 + K_{sv}[Q]$$

I_0 = Fluorescence (384 nm) intensity of unquenched pyrene

I = Fluorescence (384 nm) intensity of pyrene in presence of quencher

K_{sv} = Stern-Volmer Quenching constant

$[Q]$ = quencher concentration

concentration (Figure 4-KI and TiNO_3 ; and Figure 5- CH_3NO_2 and DMAP). We should note that all results for quenching were essentially independent of the wavelength (384 nm or 373 nm) monitored. First, in Figure 4, the ionic quenchers yield quite different results depending upon the charge of the quenching ion (Γ^- or Ti^+). In the case of Γ^- , the plot is linear, but with a low slope ($K_{sv} = 71.9$) indicating very inefficient quenching. This is quite reasonable and in accord with other results for quenching of pyrene fluorescence by Γ^- in polyelectrolyte solutions (11) : it is a direct result of charge repulsion between Γ^- and the negative charge of the carboxylate groups on the polyphosphazene I. In contrast, quenching by Ti^+ is much more efficient, but non-linear. Before providing an explanation for the results for Ti^+ quenching and its relatively high quenching efficiency it is instructive to consider the reported (10,11) attraction between Ti^+ ion and negatively charge carboxylate groups of similar polyelectrolytes. This binding of Ti^+ to the polyelectrolyte has been postulated to result in its enhanced access to the pyrene molecules located in the hydrophobic core of the polyelectrolyte and thus a larger quenching rate. [Of course, the small percentage of pyrene molecules which are in a more polar environment would naturally be accessible to quenching by free Ti^+ ions in solution]. How is this brief analysis of Ti^+ ions and their reported binding to polyelectrolytes useful in interpreting the results in Figure 4? The large quenching efficiency predicted for bound Ti^+ is obvious, at least as reflected in the initial slope of the Stern-Volmer plot at lower Ti^+ concentrations. But what about the reduced quenching efficiency at higher Ti^+ concentrations? This could well result from an inability of the polyelectrolyte to accommodate additional Ti^+ ions at higher concentrations, thus resulting in free Ti^+ ions which quench pyrene molecules

associated with the polyphosphazene polyelectrolyte by a diffusion process rather than by static quenching. If the plot for Ti^+ in Figure 4 is divided into an initial rapid static/dynamic combination quenching process (concentration of TiNO_3 ranging from 0.0 to $1.0 \times 10^{-4} \text{ M}$) and a slower primarily diffusion controlled quenching process at higher concentrations (concentration of TiNO_3 ranging from 8.33×10^{-4} to $1.67 \times 10^{-3} \text{ M}$), quenching constants of 3067 and 310 are obtained, respectively. The very large initial quenching constant (3067) for bound Ti^+ ions is similar to the value (3250) obtained by Auroa and Turro (11) for intensity quenching of the fluorescence of bound pyrene in a pyrene substituted poly(acrylic acid) polymer. Interestingly, the Stern-Volmer constant obtained for quenching of pyrene in the present case at higher Ti^+ concentrations (310) is rather close (relatively) to the value obtained (11) for lifetime quenching of the bound pyrene in the poly(acrylic acid) case (642). If we assume that the 310 value for dynamic Stern-Volmer quenching of pyrene fluorescence (polyelectrolyte I solution) at higher Ti^+ ion concentrations corresponds to the lifetime quenching value for K_{sv} obtained by Aurora and Turro (642), then the difference ($3067 - 310 = 2756$; defined as the static quenching component K_s) is almost the same as the 2608 value for K_s from reference 11 for bound pyrene. Although we are comparing two quite different methods for estimating K_s for two completely different systems, agreement between the two values obtained is noteworthy. Finally, we should mention that we do not include lifetime quenching data, which in our case, due to the two component decay, is difficult to interpret.

Figure 5 shows Stern-Volmer plots for the two non-ionic quenchers CH_3NO_2 and DMAP. Both quenchers have Stern-Volmer K_{sv} quenching constants intermediate

($K_{sv} = 148.7$ for CH_3NO_2 and $K_{sv} = 133.1$ for DMAP) between the K_{sv} constants for Γ^- and Ti^+ (at higher concentrations). This seems quite reasonable in view of the non-ionic nature of both CH_3NO_2 and DMAP. The rather low value of K_{sv} for DMAP deserves comment. In the fluorescence quenching work reported by Aurora and Turro for bound pyrene in a pyrene substituted poly(acrylic acid) system (11), DMAP was found to give an unusually large K_{sv} value, approximately two orders of magnitude greater than CH_3NO_2 . In the present case for polyphosphazene I and non-bound pyrene, the K_{sv} value for DMAP is almost the same as for CH_3NO_2 . The large value reported for the DMAP-pyrene substituted poly(acrylic acid) system was attributed to pre-association of DMAP and pyrene induced by hydrophobic interactions. Apparently, in the microenvironment created by polyphosphazene I at high pH (pH = 12), the hydrophobic core in which pyrene exists is not conducive to ground state association, hence the K_{sv} constant is essentially identical to that obtained for CH_3NO_2 .

Conclusions

The results in this paper provide insight into the nature of the hydrophobic environment created by a polyphosphazene polyelectrolyte in aqueous media. Using ANS, TNS, and pyrene fluorescent probes the polyphosphazene polymer is depicted as providing a microenvironment at high pH (pH = 12) which is similar in polarity to that of methanol. Interestingly, even in the absence of added NaCl electrolyte, a hydrophobic environment capable of solubilizing pyrene is generated. The hydrophobic environment is no doubt created by the methyl and phenyl substituents attached to the parent phosphazene backbone. Steady-state fluorescence quenching for pyrene by a negatively

charged ionic species suggests that the microenvironment is "protected" by the negatively charged carboxylate salt species on the polyphosphazene, which are present on 50 percent of the phosphazene repeat units. Conversely, the negatively charged carboxylate groups can accommodate and bind a limited concentration of positively charged ions (Ti^+) and enhance quenching of pyrene (at least for low Ti^+ concentrations). Uncharged quencher species (CH_3NO_2 and dimethylaminopyridine) are unaffected by the negative charge on the phosphazene in high pH solutions. Unfortunately, due to the limited pH range in which the water-soluble polyphosphazene is soluble, it is impossible to conduct a comprehensive investigation of the effect of pH on the polymer microenvironment in solution using fluorescent probes. The composite results in this paper, however, clearly illustrate the potential of water-soluble polyphosphazenes and their ability to form a moderately hydrophobic environment in aqueous media, even at high pH and in the absence of added electrolyte. By selective substitution of side groups, it should be possible to generate polyphosphazene polyelectrolytes which display a variety of properties in aqueous media.

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Figure Captions

- Figure 1 Plot of relative fluorescence intensity versus emission wavelength for ANS; $\lambda_{\text{ex}} = 377\text{nm}$; polyphosphazene at 0.19mg/mL ; ANS at $1 \times 10^{-5}\text{ M}$; for NaCl concentrations of: (a) 0.00 M , (b.) 0.17 M , (c) 0.34 M and (d) 0.50 M , in water at $\text{pH} = 12$.
- Figure 2 Plot of relative fluorescence intensity versus emission wavelength for TNS; $\lambda_{\text{ex}} = 345\text{ nm}$; polyphosphazene at 0.19mg/mL ; TNS at $1 \times 10^{-5}\text{ M}$; for NaCl concentrations of: (a) 0.00 M , (b) 0.17 M , (c) 0.34 M and (d) 0.50 M , in water at $\text{pH} = 12$.
- Figure 3 Plot of relative fluorescence intensity versus emission wavelength for pyrene; $\lambda_{\text{ex}} = 336\text{ nm}$; polyphosphazene at 0.19mg/mL ; pyrene at $5 \times 10^{-7}\text{ M}$; for NaCl concentrations of: (a) 0.10 M (no polyphosphazene), (b) 0.00 M (with polyphosphazene), (c) 0.10 M (with polyphosphazene) and (d) 0.34 M (with polyphosphazene), in water at $\text{pH} = 12$.
- Figure 4 Stern-Volmer plot of pyrene ($5 \times 10^{-7}\text{ M}$) and polyphosphazene (0.19mg/mL) for: (a) TiNO_3 and (b) KI , in water at $\text{pH} = 12$.
- Figure 5 Stern-Volmer plot of pyrene ($5 \times 10^{-7}\text{ M}$) and polyphosphazene (0.19mg/mL) for: (a) CH_3NO_2 and (b) DMAP , in water at $\text{pH} = 12$.

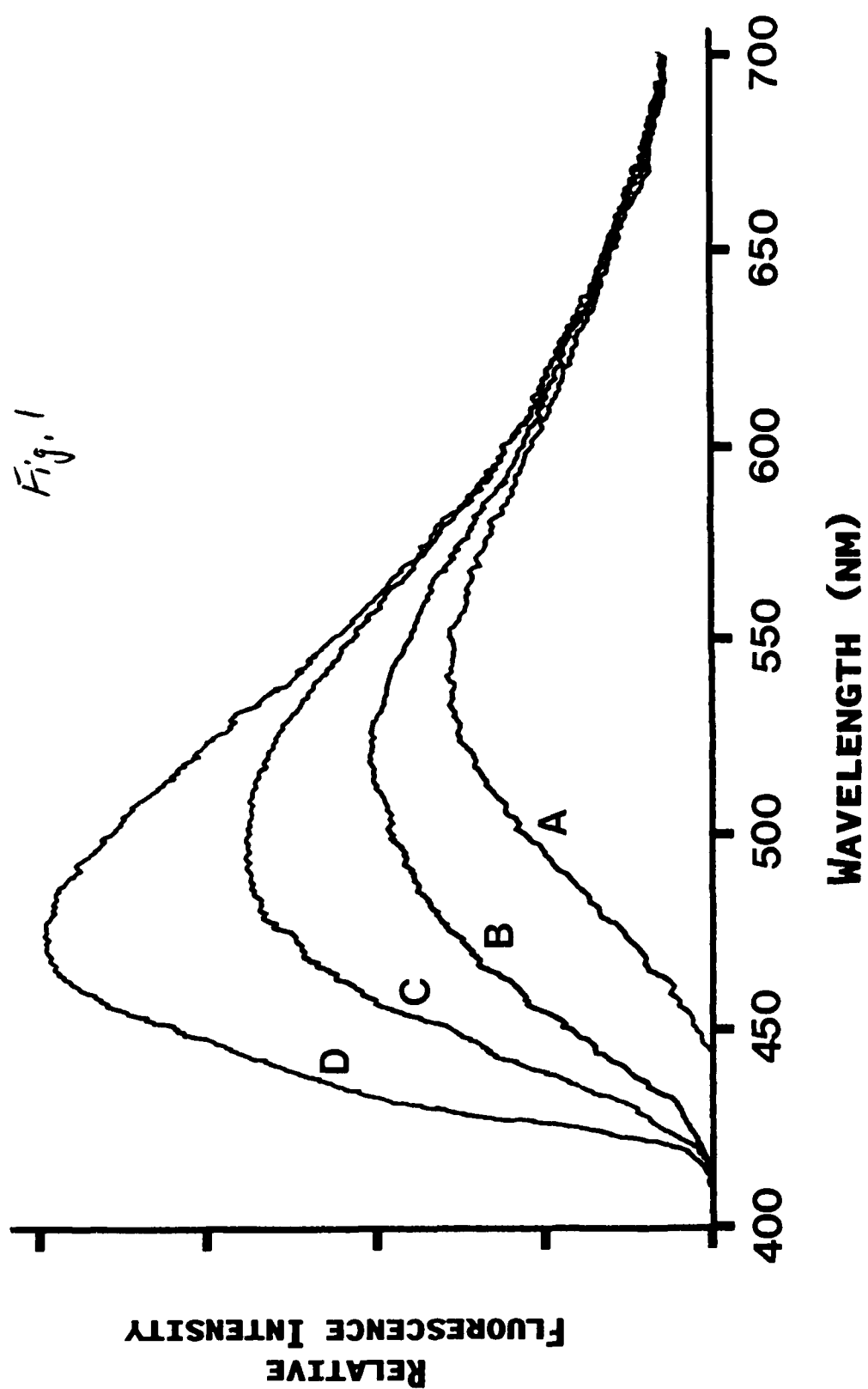


Fig. 2

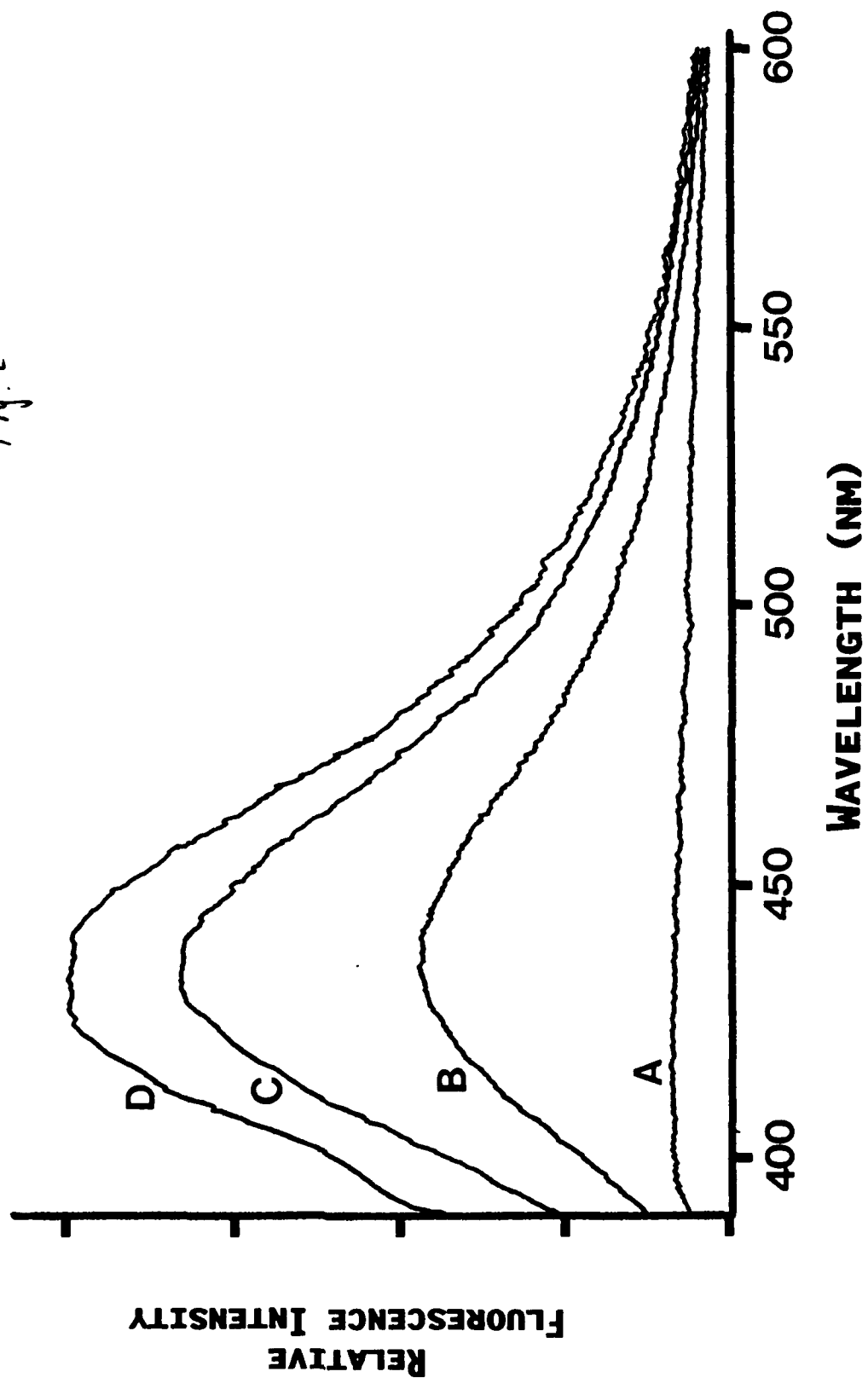


Fig. 3

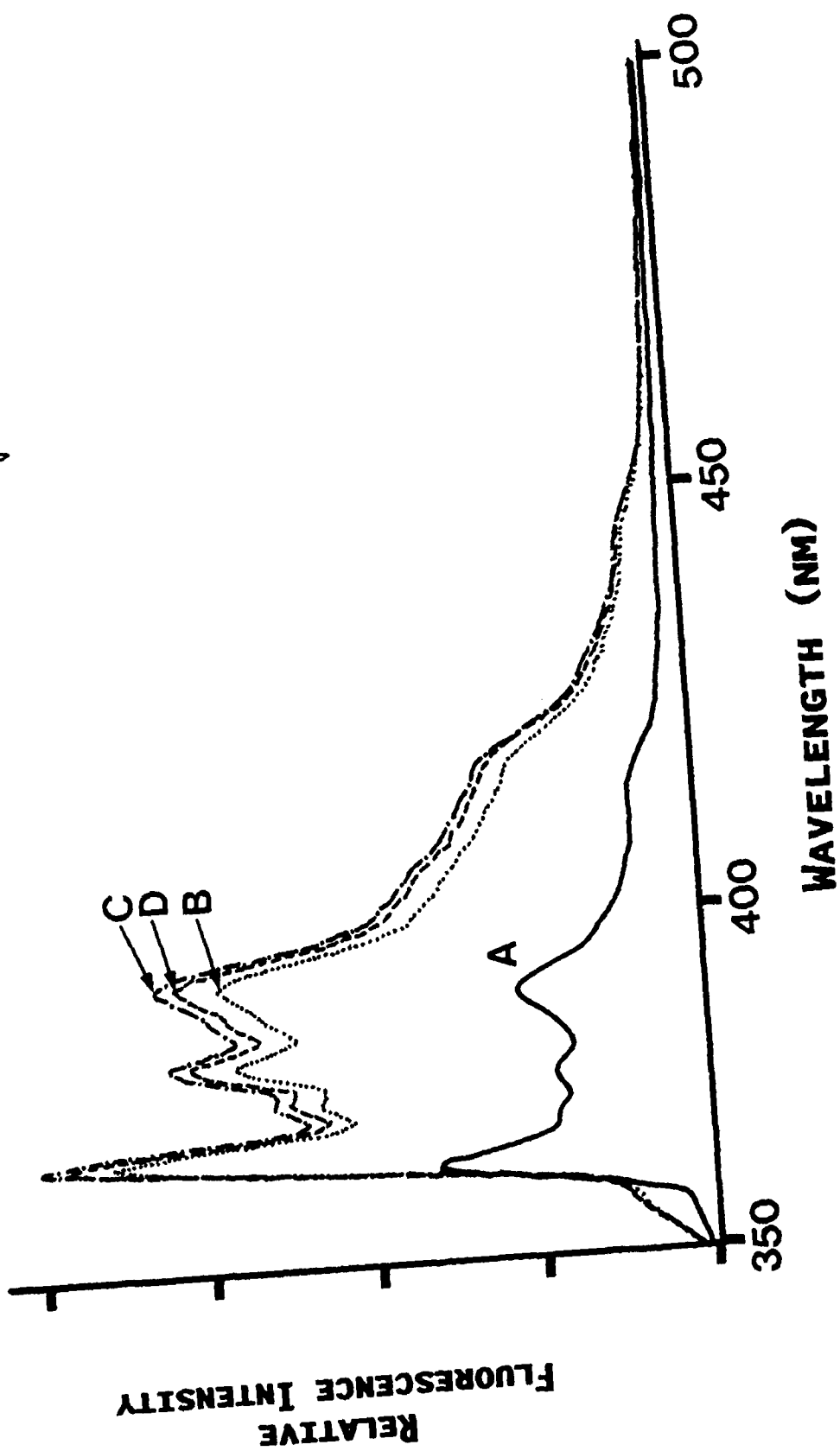


Fig. 4

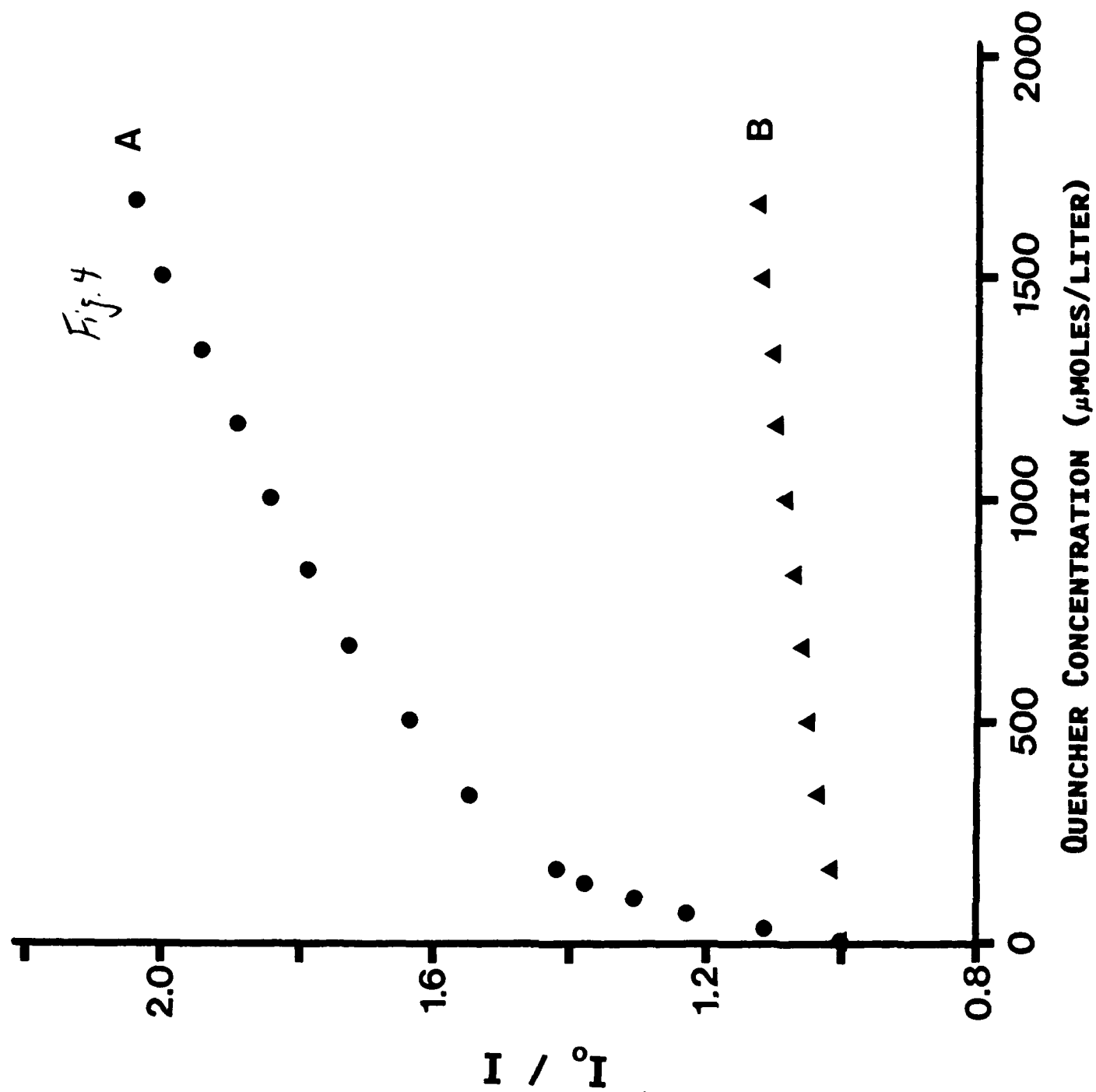


Fig. 5

